

EXHIBIT A

[Translator note "TN": A word in brackets is added by the translator in order to make the meaning clear.]

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[TN: A word with an asterisk can be read differently due to nature of Japanese.]

(54) **[Title of the invention]** Holder for exhaust gas purifying device

(57) **Abstract**

[Constitution]

A holder for an exhaust gas purifying device characterized by a constitution comprised of a blanket made by: laminating alumina fiber, for which the single fiber tensile strength is 150~400kg/mm², 5% by weight or less of shot content having a 45µm diameter or greater,

and for which the weight ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is 70/30 ~ 74/26, and; needle-punching some of the fiber to orient in the vertical direction in relation to the laminated surface.

[Effects]

According to the present invention, there can be obtained a holder in which fiber deterioration hardly occurs even for a long period of use and which exhibits stable holding ability for a long time.

Claims

[Claim 1]

A holder for an exhaust gas purifying device characterized by a constitution comprised of a blanket made by: laminating alumina fiber, for which the single fiber tensile strength is $150\sim 400\text{kg/mm}^2$, 5% by weight or less of shot content having a $45\mu\text{m}$ diameter or greater, and for which the weight ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is 70/30 ~ 74/26, and; needle-punching some of the fiber to orient in the vertical direction in relation to the laminated surface.

[Claim 2]

A holder for an exhaust gas purifying device as described in Claim 1 in which the crystallinity of the alumina fiber is 0~10%.

[Claim 3]

An internal combustion engine exhaust gas purifying device having the holder, described in Claim 1 or 2, placed between a catalyst casing and a honeycomb catalyst housed inside the catalyst casing.

[Detailed Description of the Invention]

[0001] [Industrial Field of Application]

The present invention relates to a catalyst holder used for an internal combustion engine exhaust gas purifying device. Specifically it relates to a holder that holds a honeycomb type catalyst in a catalyst casing.

[0002] [Prior Art]

For removal of nitrogen oxide contained in internal combustion engine exhaust gas, a purifying device, which houses a honeycomb type catalyst in a catalyst casing, is installed in an exhaust gas passage. In automobiles, a muffler is used as a catalyst casing and a ceramic catalyst housed in a catalyst casing in the muffler is used as a purifying device. In order to stably hold this honeycomb type catalyst in a muffler, it is proposed to use, as a holder, a formed object obtained by hardening with an organic binder, etc. ceramic fiber or ceramic fiber in which thermally expandable mineral pieces are dispersed. (Please refer to Tokkai [Publication of Unexamined Patent Application] No. 1-240715).

[0003]

Known ceramic fiber used as such holders are silica fiber, alumina-silica fiber, asbestos fiber, glass fiber, zirconia-silica fiber, etc. In diesel engines, since exhaust gas contains a large quantity of soot, some soot is collected at the muffler and then burned and removed by performing high temperature heat treatment inside the muffler. Because of this, a honeycomb type catalyst and holder are exposed to high temperatures of 800~1000°C. Under such high temperature, fiber becomes brittle caused by formation of crystalline grains and crystal growth, so there was a concern of reduction of holding ability.

[0004] [Problems that the Invention is to Solve]

The purpose of the present invention is to provide a honeycomb catalyst holder in which fiber does not become brittle under high temperature and burning and removal of an organic binder is not troublesome.

[0005] [Means to Solve the Problems]

The present invention is achieved based upon the finding that when a blanket, which is made of mullite composition alumina fiber having great strength and containing a small shot content and for which needle-punching is performed, is used as a holder, it excels in retaining strength and deterioration occurs hardly at all. Describing the present invention in more detail, the holder of the present invention is made of laminates of alumina fiber.

The fiber length and fiber diameter of alumina fiber that comprises laminates are not specifically limited, but usually the length is 20~200mm and the fiber diameter is 1~40 μ m, preferably 2~20 μ m. This fiber must be a mullite composition having a weight ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ (hereafter referred to as " $\text{Al}_2\text{O}_3/\text{SiO}_2$ ") of 70/30 ~ 74/26. When $\text{Al}_2\text{O}_3/\text{SiO}_2$ of alumina fiber is not in the above-described range, fiber deterioration, caused by crystallization and crystal growth at high temperature, occurs prematurely and it does not withstand long usage.

[0006]

The preferable crystallinity of a mullite composition alumina fiber used in the present invention is 0~10%. Here, crystallinity is expressed by a percentage (%) of peak intensity of a mullite composition alumina fiber at $2\theta=26.3^\circ$ in relation to the peak intensity at $2\theta=26.3^\circ$, measured by X-ray diffraction using $\text{CuK } \alpha$ -ray, of a completely crystallized mullite, which is sintered at 1300°C for 4 hours. Compared to alumina fiber having other compositions, crystalline grains are hard to be formed for the mullite composition alumina fiber when it is heated at temperature. Especially a low crystalline mullite composition alumina fiber, having crystallinity of 0~10%, has few crystals that become nucleus for crystal growth, so fiber deterioration does not easily occur when it is subjected to 800~1000°C heating.

[0007]

The single fiber tensile strength of alumina fiber used in the present invention is 150~400 kg/mm^2 . When it is less than 150 kg/mm^2 , sufficient surface pressure cannot be obtained [for use] as a holder. The greater the single fiber tensile strength, the greater the strength of the holder, so it is preferable, but when it exceeds 400 kg/mm^2 , fiber lacks flexibility and the holder becomes brittle. Further, the alumina fiber used in the present invention has 5% by weight or less of shot content having a diameter of 45 μ m or greater. When shot with less than 45 μ m diameter is present in the holder, it does not have an impact on retaining strength, etc., but for shot with greater than a 45 μ m diameter, fiber breakage occurs caused by its [shot] becoming a fulcrum and loses retaining strength. When shot content, with 45 μ m diameter or greater, exceeds 5% by weight, the specific

gravity of portions of the holder increases, so thermal conductivity becomes uneven, resulting in inability to evenly hold a honeycomb type catalyst.

[0008]

The blanket made by laminating alumina fiber can be produced using a generally known blanket production method. For example, an organic binder, such as: alumina sources, for instance alumina oxychloride, etc.; silica sources, for instance silica sol, etc., or; polyvinyl alcohol, etc., is mixed with water and then spun to obtain an alumina precursor. A sheet made by laminating the alumina precursor is needle-punched and then sintered at 1000~1300°C to obtain the blanket.

[0009]

Some of the alumina fiber precursors in the sheet penetrate through the sheet by needle punching and they are oriented in the vertical direction to tightly bind the sheet, so the sheet bulk density is increased and furthermore, separation of the layers and shifts between the layers can be prevented. The density of needle-punching is usually 1~50 punchings/cm². A change in the density of needle-punching enables adjustment of the blanket bulk density and strength. (Please refer to Tokkai No. 62-17060.)

In order to hold a honeycomb type catalyst in a catalyst casing using the holder of the present invention, for example: the holder is tightly wound around the entire honeycomb-type catalyst so as to be an even thickness; placed in a catalyst casing, and; secured by closely attaching to the inner wall of the casing using the retaining strength of the holder.

[0010] [Working Examples]

Next, the present invention is specifically described with reference to the working examples. However, the present invention is not limited to the following working examples so long as the main points are within its scope.

[0010] Working Example 1

In order to examine fiber deterioration for 24 hours heating at 800°C, 25g of a blanket, which has the characteristics described in Table 1, made of fiber with a fiber diameter of about 4μm and containing 4% shot having a 45μm [diameter] or greater, and which was needle-punched, was dispersed in 1.5 liters of water. It was loosened for a specific time using a home use mixer. After it was left for 30 minutes, a sedimentation volume was measured. When fiber deteriorates, fiber breaks, caused by loosening, and become shorter and the sedimentation volume becomes smaller. Thus, comparing the sedimentation volume before and after heat treatment, the degree of deterioration by heat treatment is understood. Results are shown in Table 1.

[0011] Comparative Example 1

The same operation was performed as in Working Example 1 except that a blanket, having the characteristics shown in Table 1, made of fiber having a fiber diameter of about 4μm, and needle-punched, was used. Results are shown in Table 1.

[0012] Comparative Example 2

The same operation was performed as in Working Example 1 except that a blanket, having the characteristics shown in Table 1, made of fiber having a fiber diameter of about 3μm, and needle-punched, was used. Results are shown in Table 1.

[0013] [Table 1]

	Al ₂ O ₃ / SiO ₂	Fiber		Single fiber strength (kg/mm ²)	Heat treatment	Sedimentation volume (cm ² /l)				
		Crystal- linity (%)	Content of shot with 45μm or more			Loosening time (sec)				
						30	60	90	120	150
Working										
Example 1	72/28	0	4	200	Before	72	64	62	60	54
					After	74	64	68	60	56
Comparative Example										
1	95/5	0	2	80	Before	32	19	16	15	14
					After	23	14	9	9	9
2	50/50	0	25	200	Before	64	58	56	54	52
					After	58	48	46	44	38

[0014]

As evident from Table 1, with fiber whose single fiber tensile strength is less than 150kg/mm^2 , the sedimentation volume before the heat treatment is small and fiber tends to be easily broken. Even if the single fiber tensile strength is greater than 150kg/mm^2 , when the content of shot having [a diameter] larger than $45\mu\text{m}$ exceeds 5% by weight, it is evident that breakage after the heat treatment is significant.

[0015] Working Example 2

A rectangular parallelepiped test piece of 50×50 (mm) was cut from the blanket that was made of the same fiber as that in Working Example 1, with surface density of 0.160g/cm^2 , and with needle-punching. A cycle test was conducted using this test piece to examine change in surface pressure caused by repetitions of high temperature and low temperature, i.e., change in holding ability. The surface density is a value obtained by calculation of density multiplied by thickness. Results are shown in Table 2.

[0016] Cycle Test

1. At room temperature, compress the test piece to 4.6mm in the thickness direction and measure the surface pressure.
2. Next, while expanding the thickness of the test piece to 4.9mm, heat the test piece until the center portion becomes 800°C . When the center portion of the test piece becomes 800°C , measure the surface pressure.
3. While measuring the surface pressure, hold it at 800°C for one hour.
4. Leave it cool while compressing the thickness of the test piece to 4.6mm.
5. 1 through 4 makes up one cycle. Repeat this cycle three times.

[0017] Comparative Example 3

The cycle test was conducted using a formed object containing a mineral that is available in the market as a honeycomb type catalyst holder. This mineral-containing formed object was produced by compressing the thickness of ceramic fiber, having a surface density of 0.278g/cm^2 , to about 4mm. Heating burned the organic binder in the formed object and it expanded to about 20mm in the thickness direction to exhibit the holding

ability. At the room temperature during the first cycle, the formed object was smaller than the clearance; thus no surface pressure was generated. Results are shown in Table 2.

[0018] [Table 2]

	Surface density (g/cm ²)	Temperature/ thickness	Surface pressure (kg/cm ²)		
			1 cycle	2 cycle	3 cycle
Working Example 2	0.160	Room temp. /4.6mm	1.88	1.85	1.77
		800°C/ 4.9mm	1.29→1.29	1.16→1.16	1.10→1.10
Comparative Example 3	0.278	Room temp. /4.6mm	-----	1.80	1.73
		800°C/ 4.9mm	2.56→0.29	0.11→0.00	0.00→0.00

[0019]

In Table 2, the surface pressure values at the left side show the maximum value and those at the right side show [the value] just before the temperature drop. The holder of the present invention exhibited sufficient surface pressure after being subjected to repeated heating and cooling and maintained the holding ability. It was evident that the mineral-containing formed object showed fiber deterioration after repetition of heating and cooling, and after the second and following cycles, it did not exhibit the surface pressure at 800°C and it lost the holding ability.

[0020] Working Example 3

A blanket, that was made of the same fiber as in Working Example 1 and with needle punching performed, was heat treated at 800°C for 24 hours to obtain a blanket having surface density of 0.160g/cm². From this blanket, a rectangular parallelepiped test piece of 50 x 50 (mm) was cut. It was compressed in the thickness direction at room temperature. The thickness was alternately increased and decreased from 4.6mm to 4.9mm to measure the surface pressure. One increase and decrease was viewed as one set and 10 sets were repeated. Table 3 shows the results.

[0021] Working Example 4

A blanket, having the characteristics show in Table 3, made of fiber having a fiber diameter of 4μm, and with needle punching performed, was heat treated at 800°C for 24

hours. Except for the use of this blanket, the same operation as in Working Example 3 was performed. Results are shown in Table 3.

[0022] Comparative Example 4

The same operation as in Working Example 3 was performed except for using a blanket, made of the same fiber as Comparative Example 1 and with needle punching performed, and heat treated at 800°C for 24 hours. Results are shown in Table 3.

[0023] Comparative Example 5

The same operation as in Working Example 3 was performed except for using a blanket, made of the same fiber as Comparative Example 2 and with needle-punching performed and heat treated at 800°C for 24 hours. Results are shown in Table 3.

[0024] Comparative Example 6

The same operation as in Working Example 3 was performed except for using the same mineral-containing formed object as Comparative Example 3, heat-treated at 800°C for 24 hours. Results are shown in Table 3.

[0025] [Table 3]

	Al ₂ O ₃ / SiO ₂	Fiber Crystal- linity (%)	Content of shot with 45μm or more (wt%)	Single fiber strength (kg/mm2)	Thickness	Surface pressure (kg/cm2)									
						1	2	3	4	5	6	7	8	9	10
Working Example															
3	72/28	0	4	200	4.6mm	2.92	2.43	2.31	2.27	2.22	2.21	2.16	2.12	2.12	2.07
					4.9mm	1.27	1.18	1.15	1.12	1.09	1.08	1.05	1.04	1.02	1.00
4	72/28	100	4	150	4.6mm	2.10	1.68	1.59	1.53	1.49	1.46	1.44	1.43	1.41	1.39
					4.9mm	0.81	0.75	0.72	0.70	0.68	0.66	0.64	0.67	0.64	0.63
Comparative Example															
4	95/5	0	2	80	4.6mm	1.49	1.23	1.19	1.14	1.11	1.09	1.08	1.06	1.04	1.04
					4.9mm	0.56	0.52	0.49	0.47	0.46	0.45	0.44	0.43	0.42	0.41

5	50/50	0	25	200	4.6mm	1.39	1.10	1.01	0.98	0.94	0.91	0.88	0.87	0.86	0.85
					4.9mm	0.47	0.41	0.38	0.36	0.36	0.34	0.33	0.32	0.32	0.31
6	Mineral containing formed object				4.6mm	0.61	0.60	0.59	0.59	0.60	0.59	0.58	0.57	0.57	0.58
					4.9mm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

[0026]

From Table 3, blankets, which have a high surface pressure with 4.6mm thickness for the first set and a small reduction in surface pressure after repetitions of increase and decrease of thickness, have high fiber retaining strength and are suitable for the holder.

[0027] [Effects of the Invention]

According to the present invention, there can be obtained a holder in which fiber deterioration hardly occurs after a long period of use and which exhibits stable holding ability for a long time.